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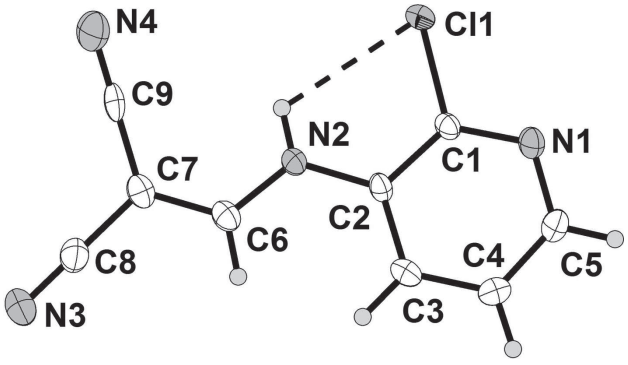
Crystal structure of 2-((2-chloropyridin-3-ylamino)methylene)malononitrile, $C_9H_5ClN_4$



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Abstract

$C_9H_5ClN_4$, monoclinic, $P2_1/c$ (no. 14), $a = 8.1178(4)$ Å, $b = 7.2367(4)$ Å, $c = 15.2585(8)$ Å, $\beta = 101.506(2)°$, $V = 878.36(8)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0466$, $wR_{ref}(F^2) = 0.1170$, $T = 100$ K.

CCDC no.: 1431816

Table 1: Data collection and handling.

Crystal:	Colourless, block, size 0.158×0.368×0.415 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	3.93 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω scans
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7339, 2002
$N(param)_{refined}$:	135
Programs:	SHELX [11], Bruker programs [12]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{iso}
H(4A)	4*e*	0.6846	0.8470	0.5411	0.018
H(5A)	4*e*	0.8671	0.8971	0.4445	0.016
H(6A)	4*e*	0.2139	0.5444	0.4288	0.013
H(3A)	4*e*	0.415(3)	0.718(3)	0.487(2)	0.015(6)
H(1N2)	4*e*	0.277(4)	0.577(4)	0.264(2)	0.025(7)

Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

Method A: a mixture of 3-amino-2-chloropyridine (1.28 g, 0.01 mol), malononitrile (0.66 g, 0.01 mol), triethylorthoformate (1.48 g, 0.01 mol), and methanol (30 mL) containing acetic acid (1 mL) was refluxed for 8 h, the reaction mixture was filtered, the filtered solid was crystallized from ethanol. **Method B:** a mixture of 3-amino-2-chloropyridine (1.28 g, 0.01 mol) and 2-(ethoxymethylene)malononitrile (1.22 g, 0.01 mole) in methanol (20 mL) containing acetic acid (1 mL) was refluxed for 12 h, the reaction mixture was filtered off, the filtered solid was crystallized from ethanol to give: Yield: 89%, m.p. = 193.4°C; IR: cm^{-1}: 3215 (NH), 3079 (CH arom.), 2975, 2864 (CH aliph.), 2218 (CN), 1614 (C = N), 759 (C—Cl) ^{1}H—NMR (DMSO-d$_6$, ppm): 7.2, 8.0 [m,

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Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	4*e*	0.51976(6)	0.67648(7)	0.19164(3)	0.0131(3)	0.0206(3)	0.0080(2)	−0.0055(2)	0.0043(2)	−0.0017(2)
N(1)	4*e*	0.7187(2)	0.8003(2)	0.3346(1)	0.0069(8)	0.0141(8)	0.0120(8)	0.0005(6)	0.0020(7)	0.0009(7)
N(2)	4*e*	0.2987(2)	0.6011(2)	0.3197(1)	0.0078(8)	0.0140(8)	0.0092(8)	−0.0015(7)	0.0034(7)	−0.0021(7)
N(3)	4*e*	−0.1660(2)	0.3525(3)	0.4286(1)	0.0164(9)	0.031(1)	0.0175(9)	−0.0093(8)	0.0069(8)	−0.0028(8)
N(4)	4*e*	−0.0895(2)	0.4870(3)	0.1578(1)	0.0103(9)	0.025(1)	0.020(1)	0.0014(8)	0.0014(7)	0.0023(8)
C(1)	4*e*	0.5709(2)	0.7225(3)	0.3058(1)	0.0066(9)	0.0098(9)	0.0090(9)	0.0015(7)	0.0028(7)	0.0012(7)
C(2)	4*e*	0.4524(2)	0.6831(3)	0.3583(1)	0.0063(9)	0.0101(9)	0.0107(9)	−0.0004(7)	0.0034(7)	−0.0003(7)
C(3)	4*e*	0.4957(3)	0.7335(3)	0.4483(1)	0.013(1)	0.018(1)	0.0100(9)	−0.0024(8)	0.0056(8)	−0.0010(8)
C(4)	4*e*	0.6522(3)	0.8134(3)	0.4799(1)	0.014(1)	0.021(1)	0.0088(9)	−0.0024(9)	0.0013(8)	−0.0015(8)
C(5)	4*e*	0.7601(3)	0.8438(3)	0.4220(1)	0.0093(9)	0.018(1)	0.012(1)	−0.0025(8)	−0.0003(8)	0.0006(8)
C(6)	4*e*	0.1844(2)	0.5410(3)	0.3654(1)	0.0093(9)	0.0115(9)	0.0120(9)	0.0009(8)	0.0041(7)	0.0009(7)
C(7)	4*e*	0.0287(3)	0.4752(3)	0.3278(1)	0.0092(9)	0.0123(9)	0.015(1)	0.0002(8)	0.0046(8)	0.0002(8)
C(8)	4*e*	−0.0788(3)	0.4075(3)	0.3837(1)	0.0099(9)	0.018(1)	0.014(1)	−0.0019(8)	0.0023(8)	−0.0030(8)
C(9)	4*e*	−0.0362(2)	0.4800(3)	0.2333(1)	0.0047(9)	0.013(1)	0.019(1)	−0.0008(7)	0.0034(8)	0.0007(8)

3H, Ar—H], 8.1 [s, 1H, CH, D_2O-exchangeable], 10.9 [s, 1H, NH, D_2O-exchangeable]. ^{13}C—NMR (DMSO-d_6, ppm): 55.6, 113.7(2), 122.1, 124.8, 136.7, 140.3, 146.9, 160.4. Anal. Calcd. for $C_9H_5ClN_4$ (204.62, %): C, 52.83; H, 2.46; N, 27.38. Found (%): C, 52.48; H, 2.13; N, 27.71.

Experimental details

The hydrogen atoms H4A, H5A and H6A were idealized and refined using a riding model (AFIX 43 option of the SHELX program [11]).

Discussion

Pyridine derivatives were shown antibacterial [1], antimalarial [2], anticonvulsant [3], and cytotoxic agents [4–6]. These findings led us to continue our work on the synthesis of biologically active compounds [7–10]. The aim of this work was to, synthesize the corresponding compound having a biologically active methylenemalononitrile moiety. The crystal structure of target compound contains one molecule in the asymmetric unit. There is one intramolecular N—H$\cdots$Cl hydrogen bond (figure). The crystal structure is stabilized by three intermolecular hydrogen bonds, of which N1, N3 and N4 work as hydrogen bond acceptors and N2, C6 and C4 work as hydrogen bond donors. The distance of the interactions between N2—H1N2$\cdots$N1^{i} is 2.51(3) Å, C4—H4A$\cdots$N4^{ii} is 2.58 Å and C6—H6A$\cdots$N3^{iii} is 2.4 Å and the angles are 138(3)°, 145° and 151°, respectively. Symmetry codes: (i) $-x+1$, $y-1/2$, $-z+1/2$; (ii) $x+1$, $-y+3/2$, $z+1/2$; (iii) $-x$, $-y+1$, $-z+1$.

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